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(72) Inventors YOSHIHIRO TODANI and TOSHIO OHKAWA

(19)

(54) SURFACE MODIFICATION OF RUBBER ARTICLES

(71) We, NIPPON ZEON CO LTD, a Japanese Body Corporate of 6—1, 2-chome, Marunouchi, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the treatment of surfaces of shaped rubber articles, and is an improvement in or modification of the invention described in our Application No. 44202/72 (Serial No. 1,389,886).

Application No. 44202/72 (Serial No. 1,389,886) discloses and claims a process for modifying the surface properties of a shaped article whose surface comprises a rubber containing ethylenic double bonds, which process comprises contacting the surface of the article with an alkyl hypohalite or a halogen-substituted alkyl hypohalite. It is further disclosed that as a result of this process the treated surface has a reduced friction factor and improved ozone resistance.

We have now discovered that additional results of this process are that the shaped article has reduced permeability to hydrocarbons and halogenated hydrocarbons which are volatile liquids at room temperature, e.g. petrol and the so-called "Freons" ("Freon" is a Registered Trade Mark) e.g. dichlorodifluoromethane, and that it can be more firmly bonded to other surfaces e.g. of metal, fibre, wood, glass, rubber (vulcanised or unvulcanised), leather, concrete or synthetic resin, especially when an epoxy bonding agent is employed.

In its first aspect the present invention provides apparatus which contains a hydrocarbon or halogenated hydrocarbon in contact with a shaped article composed of a rubber containing ethylenic double bonds, wherein the surface of the said article which is in contact with the hydrocarbon or halogenated hydrocarbon has been treated by contacting it with an alkyl hypohalite or a halogen-substituted alkyl hypohalite.

In its second aspect the present invention provides a process for preparing an article which comprises contacting an alkyl hypohalite or a halogen-substituted alkyl hypohalite with a shaped article of a rubber containing ethylenic double bonds, and bonding a coating or another article to the treated surface of the said shaped article.

The shaped articles which are used in the present invention may be composed, for example of natural rubber, polyisoprene, polybutadiene, butadiene-isoprene copolymer, styrene-butadiene copolymer, acrylonitrile-butadiene copolymer, acrylonitrile-butadiene-isoprene ternary copolymer, ethylene-propylene-diene ternary copolymer, polychloroprene, epichlorohydrin-unsaturated epoxide copolymer or isobutylene-isoprene copolymer rubbers, optionally blended with other rubbers and/or conventional additives, as well as vulcanisates of such blends. As the additives, reinforcing agents, fillers, softeners, plasticisers, anti-oxidants and other known additives to facilitate processing, can be named, suitable additives being selected according to the intended utility of the rubber articles.

As the alkyl hypohalite to be used for the surface treatment, tertiary alkyl hypohalites, such as tertiary butyl hypohalite and tertiary amyl hypohalite, are more preferable to normal or secondary alkyl hypohalites, because of their higher stability. The most preferred are tertiary butyl hypochlorite and tertiary butyl hypobromite. Halogen-substituted alkyl hypohalites, for example, di- or tri-chloromethyl hypochlorite, di- or tri-fluoromethyl hypochlorite, can also be used. The hypo-

nalites may be used as they are, or as solutions in organic solvents, for the surface treatment of the shaped rubber articles. It should be noted, however, that although the organic solvent can be one which may swell the rubber surfaces, it must not dissolve the rubber surface. Suitable solvents include aliphatic hydrocarbons such as heptane, n-hexane, and cyclohexane; aromatic hydrocarbons such as benzene, nitro-benzene, toluene and xylene; halogenated benzenes; ethers such as diethyl-ether and dioxane; esters such as ethyl acetate; ketones such as methyl ethyl ketone and cyclohexanone; chlorinated hydrocarbons such as ethyl chloride, chloroform, and carbon tetrachloride; tertiary alcohols such as tertiary butyl alcohol; and carbon disulphide. Those solvents may be used as mixtures. When an alkyl hypohalite is used in the form of a solution dissolved in these solvents, the concentration of the alkyl hypohalite in the solution is not limited particularly but selected suitably according to the proportions to be imparted to the shaped articles of rubber. Generally, it is preferable that the concentration be at least 0.5% by volume.

The contacting of the rubber article with the hypohalite can be effected by immersion or by coating or spraying hypohalite onto the article. In the former embodiment, the immersion time varies depending on such factors as type of rubber, concentration of the alkyl hypohalite solution, type of solvent, and the intended utility of rubber articles, but generally it does not exceed several minutes, normally ranging from one second to ten hours, preferably from three seconds to sixty minutes. The temperature at which the alkyl hypohalite is contacted with the surface of shaped articles of rubber is 0° to boiling point of the alkyl hypohalite, preferably 0 to 30°C.

The mechanism by which the favorable results are achieved is not yet fully clear. Presumably, however, they result from the introduction of halogen and alkoxy groups into the rubber by reaction of the double bonds thereof with the hypohalite.

The invention is illustrated in the following Examples, in which parts and percentages are by weight.

Example 1.

100 parts of acrylonitrile-butadiene copolymer rubber (Nipol 1042: product of Nippon Zeon Co), 5 parts of zinc oxide, 1 part of stearic acid, 1.5 parts of sulphur, 40 parts of FEF carbon black, 1.5 parts of dibenzothiazyl disulphide, and 0.5 part of diphenyl guanidine were milled with 8-inch rolls and hot-pressed at 150°C for 30 minutes. The 2 mm sheets obtained were immersed in a 25 volume % tertiary butyl alcohol solution of tertiary butyl hypochlorite at normal temperature (about 25°C) for 30 minutes. Thereafter the sheets were washed first with methyl alcohol and then with water, and dried at room temperature.

The sheet obtained was cut into a circular shape with a diameter of 63 mm. The amount (g) of a gasoline permeated through the cut sheet per cm^2 a day at 40°C was measured (the gasoline is a ASTM Fuel B, a mixture of isooctane and toluene with a volume ratio of 70 to 30). It was found to be 4.2×10^{-3} g/day × cm^2. On the other hand, in the case of the untreated sheet, the amount was 13.5×10^{-3} g/day × cm^2.

Example 2.

100 parts of a blend consisting of acrylonitrile-butadiene copolymer rubber and polyvinyl chloride, a weight ratio being 70 to 30 (Nipol 1203J: product of Nippon Zeon Co), 5 parts of zinc oxide, 1 part of stearic acid, 0.3 part of sulphur, 40 parts of FEF carbon black, 2.5 parts of tetramethylthiuram disulphide, and 2.0 parts of cyclohexylbenzothiazyl sulphenamide were milled with 8-inch rolls and hot-pressed at 150°C for 30 minutes. The 2 mm sheets obtained were immersed in tertiary butyl alcohol solutions of tertiary butyl hypochlorite in the concentrations of 20 volume % (sample 1), 25 volume % (sample 2) and 30 volume % (sample 3) at normal temperature (about 25°C) for 30 minutes. The sheets were washed first with methyl alcohol and then with water, and dried at room temperature. The amount of gasoline permeated through the sheets so obtained was measured. The results are shown in Table 1.

TABLE 1

	Amount of gasoline permeated (10^{-3} g/day×cm^2)
Control (untreated)	9.38
Sample 1	3.53
Sample 2	2.66
Sample 3	2.43

The physical and chemical properties f the control and samples 1, 2 and 3 were inspected. The results are shown in Table 2, which demonstrates that the other properties of the treated samples were not substantially changed.

TABLE 2

	Control	Sample 1	Sample 2	Sample 3
Normal physical properties				
Tensile strength (Kg/cm^2)	180	168	178	165
100% modulus (Kg/cm^2)	49	49	51	53
300% modulus (kg/cm^2)	140	138	142	140
Hardness (JIS)	77	77	76	78
Tear strength (Kg/cm)	64	67	71	69
Heat ageing test (Test tube 120°×70 hrs)				
Change ratio of tensile strength (%)	+ 8.3	+14.9	+ 5.6	+12.7
Change ratio of elongation (%)	−50.0	−46.7	−45.7	−46.3
Change ratio of 100% modulus (%)	+100.2	+102.0	−117.6	+84.9
Change of hardness	+ 4	+ 6	+ 7	+ 5
Oil resistance test (Ratio (%) of volume change caused by immersion)				
ASTM 3 oil (100°C×70 hrs)	+12.6	+ 9.9	+ 9.0	+ 5.9

Control Example.

Example 2 was repeated with a treating agent shown in Table 3 instead of the treating agent of this invention used in Example 2. The results are shown in Table 3.

TABLE 3

Treating Agent	Amount of gasoline permeated (10^{-3} g/day×cm^2)
Hypochlorous acid aqueous solution of 2% chlorine content	7.11
2% aqueous solution of bromine	6.20

Even though the treating agents used in the controls had some useful effect they were inferior to those used in the present invention.

Example 3.

100 parts of a blend (Nipol 1203J: product of Nippon Zeon Co.) consisting of acrylonitrile-butadiene copolymer rubber and polyvinyl chloride, a weight ratio being 70 to 30, 5 parts of zinc oxide, 1 part of stearic acid, 0.3 part of sulphur, 40 parts of FEF carbon black, 2.5 parts of tetramethylthiuram disulphide, and 2.0 parts of cyclohexylbenzothiazyl sulphenamide were milled with 8-inch rolls, and hot-pressed at 150°C for 30 minutes.

The 2 mm sheets obtained were treated with a toluene solution of tertiary butyl hypochlorite at normal temperature (about 25°C) under conditions of concentration and treating times shown in Table 4.

TABLE 4

Sample No.	Concentration of tertiary butyl hypochlorite (volume %)	Treating time (second)
1	5	30
2	15	30
3	25	30
4	25	30

The amount of gasoline permeated through sheets so treated and untreated (control) was measured in the same manner as in Example 1. The results are shown in Table 5.

TABLE 5

	Amount of gasoline permeated (10^{-3} g/day×cm^2)
Control (untreated)	22.4
Sample 1	2.7
Sample 2	0.6
Sample 3	0.6
Sample 4	0.7

Example 4.

Example 1 was repeated with a rubber containing carbon-to-carbon double bonds shown in Table 6 instead of the acrylonitrile-butadiene copolymer rubber used in Example 1. The results are shown in Table 6.

TABLE 6

Rubber	Treatment	Amount of gasoline permeated (10^{-3} g/day×cm^2)
Acrylonitrile-butadiene-isoprene ternary copolymer*	untreated	14.2
	treated	4.7
Acrylonitrile-isoprene copolymer**	untreated	9.2
	treated	2.3

* Product of Nippon Zeon Co., Nipol DN-1201.

** Product of Polymer Corp., Ltd., Polysar Krynac 833 ("Polysar" and "Krynac" are Registered Trade Marks).

Example 5.

100 parts of styrene-butadiene rubber (Nipol 1502: product of Nippon Zeon Co), 5 parts of zinc oxide, 1.8 parts of sulphur, 1.5 parts of stearic acid, 40 parts of HAF carbon black, 1.5 parts of dibenzothiazyl disulfide, and 0.7 part of diphenyl guanidine were milled with 6-inch rolls, and the blend obtained was pressed and vulcanised at 150°C for 20 minutes to prepare a shaped article of rubber having a thickness of 2 mm.

The surface of the shaped article was washed with acetone, immersed in a treating agent shown in Table 7 for 30 seconds, and left standing for a day. On the other hand, the surface of a steel SAE—1020 also was washed with methyl ethyl ketone.

Thereafter, an epoxy bonding agent (Sanyu resin A—460 produced by Sanyu Kogyo K.K.) was coated on the shaped article of rubber and steel. Both were bonded under pressure at 80°C and 100—200 g/cm^2 for an hour. The composite article obtained was subjected to the 180° peeling test according to JIS K—6301. The results are shown in Table 7.

TABLE 7

Treating Agent	Peel strength (Kg/cm)
untreated	not bonded
25 volume % tertiary butyl hypochlorite solution in tertiary butyl alcohol	3.2
Tertiary butyl hypochlorite	20.0 (rubber breakage)

Superior bonding strength is obtained using tertiary butyl hypochlorite on the surface of the vulcanised rubber having a great chlorination capacity as a treating agent.

Example 6.

100 parts of styrene-butadiene rubber (Nipol 1502: product of Nippon Zeon Co.), 5 parts of zinc oxide, 1.8 parts of sulphur, 1.5 parts of stearic acid, 40 parts of HAF carbon black, 1.5 parts of dibenzothiazyl disulphide, and 0.7 part of diphenyl guanidine were milled with 6-inch rolls, and the blend obtained was pressed and vulcanised at 150°C for 15 minutes to prepare a shaped article of rubber having a thickness of 2 mm. The shaped article was washed with acetone, immersed in a mixed solution of a 0.1 mol tertiary butyl hypochlorite and 90 g tertiary butyl alcohol at room temperature for 2 minutes, taken out, washed with water, and dried.

On the other hand, 100 parts of vinyl chloride resin (Zeon 131: product of Nippon Zeon Co.), 60 parts of dioctyl phthalate, 3 parts of stabiliser (S—67J: product of Katsuta Kako K.K.), and 40 parts of epoxy resin [Epikote: product of Shell International Chemicals Corp. ("Epikote" is a Registered Trade Mark)] were milled with a mixer. The blend was further milled with 4 parts of diethylene triamine for 5 minutes and defoamed by a vacuum defoamation machine.

The sol obtained was coated on said shaped article of rubber and heated in a hot blast circulation-type oven at 180°C for 10 minutes. The bonding strength of the composite article obtained was measured. The results are shown in Table 8.

TABLE 8

Treatment of shaped rubber article by tertiary butyl hypochlorite	Untreated	treated
Bonding strength (Kg/cm)	2	>5
Breakage	surface breakage	Breakage of vinyl chloride resin sheet

Example 7.

Example 5 was repeated using a rubber shown in Table 9 instead of the styrene-butadiene rubber used in Example 5. Results are shown in Table 9.

TABLE 9

Treating agent \ Rubber	Acrylonitrile* butadiene rubber	Polybutadiene** rubber
Untreated	not bonded	not bonded
25 volume % tertial butyl hypochlorite solution in tertiary butyl alcohol	2.5	3.0
tertiary butyl hypochlorite	19.0 (rubber breakage)	18.5 (rubber breakage)

* Product of Nippon Zeon Co.: Nipol 1042AL
** Product of Nippon Zeon Co: Nipol BR 1220

WHAT WE CLAIM IS:—

1. Apparatus which contains a hydrocarbon or halogenated hydrocarbon in contact with a shaped article composed of a rubber containing ethylenic double bonds, wherein the surface of the said article which is in contact with the hydrocarbon or halogenated hydrocarbon has been treated by contacting it with an alkyl hypohalite or a halogen-substituted alkyl hypohalite.

2. Apparatus according to claim 1 wherein the alkyl hypohalite is a tertiary alkyl hypohalite.

3. Apparatus according to claim 2 wherein the alkyl hypohalite is tertiary butyl hypochlorite.

4. Apparatus according to claim 2 wherein the alkyl hypohalite is tertiary butyl hypobromite.

5. Apparatus according to any one of the preceding claims wherein the hydrocarbon is petrol.

6. Apparatus according to any one of claims 1 to 4 wherein the halogenated hydrocarbon is dichlorodifluoromethane.

7. A process for preparing an article which comprises contacting an alkyl hypohalite or a halogen-substituted alkyl hypohalite with a shaped article of a rubber containing ethylenic double bonds, and bonding a coating or another article to the treated surface of the said shaped article.

8. A process according to claim 7 wherein the alkyl hypohalite is a tertiary alkyl hypohalite.

9. A process according to claim 8 wherein the alkyl hypohalite is tertiary butyl hypochlorite.

10. A process according to claim 8 wherein the alkyl hypohalite is tertiary butyl hypobromite.

11. A process according to any one of claims 7 to 10 wherein the other article is composed of rubber.

12. A process according to any one of claims 7 to 10 wherein the other article is composed of metal.

13. A process according to any one of claims 7 to 10 wherein the other article is composed of wood or is a fibrous material.

14. A process according to any any one of claims 7 to 13 wherein the bonding is effected with the aid of an epoxy bonding agent.

15. A process according to claim 7 substantially as hereinbefore described.

16. An article prepared by a process as claimed in any one of claims 7 to 15.

J. A. KEMP & CO.,
Chartered Patent Agents,
14 South Square,
Gray's Inn,
London WC1R 5EU.

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